*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2013.848670

53 (2015) 697–708
January

Taylor & Francis
Taylor & Francis Group

# Removal of chloro-organics and color from pulp and paper mill wastewater by polyaluminium chloride as coagulant

Ashutosh Kumar Choudhary*, Satish Kumar, Chhaya Sharma

*Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur, UP 247001, India*
*Tel. +91 9045884924; email: akchoudhary.env@gmail.com*

Received 29 May 2012; Accepted 11 September 2013

ABSTRACT

This study evaluates the effectiveness of polyaluminium chloride (PAC) as a coagulant for the treatment of pulp and paper mill wastewater. The wastewater was characterized for different chloro-organic compounds, i.e. adsorbable organic halides (AOX), chlorophenolics, and chlorinated resin and fatty acids (cRFA). Four categories of chlorophenolics (chlorophenols, chlorocatechols, chloroguaiacols, and chlorosyringaldehyde) and four cRFA were detected in the wastewater. For coagulation studies, optimization of the process variables including initial pH, coagulant dosage, time, and initial organic load was done in terms of chemical oxygen demand and color removal efficiency. Under optimized conditions (pH 8.0, PAC dose 1.5 g/L, time 90 min.), the removal efficiency for AOX, chlorophenolics, and cRFA was 66, 41, and 87%, respectively. The chlorophenolics, i.e. 2,6-dichlorophenol, 3,4-dichlorophenol, 3,4,6-trichloroguaiacol, tetrachloroguaiacol, and 2,6-dichlorosyringaldehyde were not detected after treatment studies. Among different parameters, highest removal of color was observed from wastewater by PAC.

*Keywords:* AOX; Polyaluminium chloride; Coagulation; Chlorophenolics; Chlorinated resin and fatty acids; Pulp and paper mill wastewater

## 1. Introduction

The pulp and paper mills discharge large volumes of wastewater having high color and organic load, i.e. biochemical oxygen demand (BOD) and chemical oxygen demand (COD), to the environment which may cause deleterious environmental impacts. In pulp and paper mills, wood preparation, pulping, pulp washing, bleaching, and coating operations are the major source of pollution [1]. Wastewater of paper mills also contains adsorbable organic halides (AOX) and chlorinated organic compounds which causes toxicity in receiving water bodies [2,3]. Pulping, bleaching, and chemical recovery sections are the major source of color, mainly due to lignin and its derivatives. Wastewater originating from the E (extraction) stage of bleaching section is highly colored and typically accounts for 80% of the color, 30% of BOD, and 60% of COD of the mills total pollution load. The high load of color is not only esthetically unacceptable but also inhibits the natural process of photosynthesis in the wastewater receiving streams due to absorbance of sun light. This leads to the adverse effects on the aquatic living organisms [4].

Among the various sections of paper mill, bleaching section wastewater accounts for the largest fraction

---

*Corresponding author.

of toxicity [2]. Chlorobleaching (using $Cl_2$, $ClO_2$, or other chlorine compounds such as sodium or calcium hypochlorite) of wood pulp causes the formation of chloro-organics [5–7]. More than 500 different chloro-organics have been identified including chlorate, chloroform, chlorophenolics (chlorophenols (CP), chlorocatechols (CC), chloroguaiacols (CG), chlorosyringols (CS), chlorosyringaldehydes (CSA), and chlorovanillins), chlorinated resin and fatty acids (cRFA), chlorinated hydrocarbons, dioxins and furans, etc. [8]. The chloro-organics which adsorbed to activated charcoal are estimated collectively as AOX. Chlorophenolics are formed primarily as a result of chlorination of the lignin remaining in the pulp after pulping process [5,9]. The nature and concentration of chlorophenolics formed depends upon the nature of the residual lignin remaining after pulping and pulp bleaching conditions [10]. These compounds are hydrophobic in nature and have been shown to bioaccumulate in aquatic organisms [11]. Toxicity of chlorophenolics depends on the position of chlorine atoms relative to the hydroxyl group on benzene ring and the number of chlorine atoms substituted on the phenol. Many authors reported the presence of toxic pollutants in aquatic organisms and their toxic effect on fish such as mutagenicity, respiratory stress, liver damage, genotoxic, and lethal effects when exposed to paper mill wastewaters [5,12,13]. Resin and fatty acids occur naturally in plants and trees and their purpose is to protect wood against insect and microbial damage. The cRFA found in bleach plant wastewater originate from the fibrous raw material and their amount depends on the type of wood species, bleaching chemical charge applied, and on the degree of washing of the unbleached pulp. cRFA are the major contributors for the toxicity to aquatic organisms [14].

The conventional treatment for Indian pulp and paper mills includes primary and secondary treatment (anaerobic process, activated sludge process, aerated lagoons, etc.). Some of the pollutants in paper mills wastewater are recalcitrant; hence, conventional treatment processes are not adequate to meet the regulatory wastewater standards for being discharged into receiving wastewater bodies. It has been observed that the secondary treated wastewater still contains high organic load, color, and chlorinated toxic compounds that impart toxicity to the wastewater. Therefore, to meet discharge limits and to protect wastewater receiving bodies, paper mills has to use additional treatment processes before or after secondary treatment to meet the wastewater discharge standards.

Coagulation-flocculation processes are widely used in water and wastewater treatment. These processes are effective for removing high concentration organic pollutants, and color from wastewater of different origins [15–22]. Coagulation process generally includes four different mechanisms for the destabilization of colloidal particles present in the wastewaters. These processes are charge neutralization/destablization, adsorption, enmeshment in precipitate, and complexation/precipitation [23]. In recent years, polymerized forms of metal coagulants such as polyaluminium chloride (PAC) have been used increasingly for water and wastewater treatment due to low cost, better coagulation performance than the conventional coagulants (such as alum, $FeCl_3$), wider availability, and effectiveness over a wide pH range [24–27]. These products are claimed to be superior to conventional coagulants because of lower alkalinity consumption and lesser sludge production [26]. PAC is made by partial hydrolysis of acid aluminum chloride solution due to which many species have been proposed to form during hydrolysis. Generally, accepted species include the monomers ($Al^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^+$, amorphous $Al(OH)_3$ and $Al(OH)_4^-$), a dimmer ($Al_2(OH)_2^{4+}$), a trimer ($Al_3(OH)_4^{5+}$), and a tridecamer ($Al_{13}O_4(OH)_{24}^{7+}$, denoted by $Al_{13}$) [28]. Among these species, it seems that the $Al_{13}$ species is the most effective and stable polymeric Al species for water and wastewater treatment [29,30]. The higher the valence of the counterion, more will be the destabilizing effect by coagulant [31]. Studies on the coagulation-flocculation process for the treatment of paper mill wastewaters have been reported by several researchers [20,32,33]. They reported that PAC is capable of removing high color and COD from paper mill wastewater. To date, there is no reported literature on the use of PAC for the removal of chloro-organic (AOX, chlorophenolics, and cRFA) from paper mill wastewater.

The main objective of the present study was to optimize the process variables (initial pH of the wastewater, PAC dose, slurry settling time, and initial organic load) for the treatment of pulp and paper mill wastewater by PAC as coagulant. Optimization of the process parameters was done in terms of COD and color removal efficiency. The removal efficiency for other parameters such as AOX, chlorophenolics, cRFA, and BOD was determined under optimized conditions.

## 2. Materials and methods

### 2.1. Wastewater and chemicals

For coagulation-flocculation studies, wastewater samples (after primary treatment) were collected from a paper mill which uses $OCE_{OP}HH$ (O-oxygen delignification stage, C = chlorination stage, $E_{OP}$-$H_2O_2$- and $O_2$-reinforced extraction stages, and H-hypochlorite stage) bleaching sequence for brightening the mixed hardwood (Eucalyptus and Poplar) kraft pulp. The wastewater samples were collected in clean containers and stored (1 day) in a refrigerator below 4℃ till use.

The CP used were obtained from the Aldrich (Milwaukee, USA) and Sigma (St. Louis, USA). The CC, CG, and CSA were supplied by Helix Biotech Corporation (Richmand, B.C. Canada). The cRFA used were obtained from the Aldrich Chemical Company (Milwaukee, USA) and Sigma Chemical Company (St. Louis, USA). All the standards were of highest purity commercially available. Solvents, i.e. acetone, *n*-hexane, methanol, tertiary butyl methyl ether, used were of HPLC grade and other solvents i.e. ethanol and diethyl ether used were of laboratory grade. Analytical grade acetic anhydride was used after double distillation. n-methyl-n-nitrosotoluene-p-sulphonamide was supplied by Aldrich (USA). Stock solutions of individual standard of chlorophenolics and cRFA were prepared in acetone/water (10:90) and methanol/diethyl ether (10:90) solutions, respectively. PAC (commercial grade) for coagulation-flocculation studies was obtained from Punjab Alkalies (Chandigarh, India). Other reagents used for experimental studies were of analytical reagent grade. The pH of the aqueous solutions/wastewaters was adjusted with 1 M $H_2SO_4$ or 1 M NaOH solution.

### 2.2. Experimental procedures

All the coagulation-flocculation experiments were carried out in 500 mL borosilicate glass beaker. A 10% solution of PAC was used as stock solution throughout the experiments. The initial pH of the paper mill wastewater was adjusted using solution of either NaOH or $H_2SO_4$. Each experiment was performed by adding a known amount of the coagulant into a beaker containing 250 mL of wastewater of known initial pH, COD, and color concentration. The mixture was then flash agitated for 1 min followed by gentle mixing to facilitate flocculation for 5 min and further settling for 120 min. After sedimentation, supernatant sample was withdrawn from a point 3 cm below the surface of the wastewater sample and analyzed for COD and color. For optimization of the coagulation dosage, PAC dosages were varied from 0.5 to 4.5 g/L at pH 7. To optimize initial pH, the coagulation of paper mill wastewater by PAC was studied over a pH range 4–9 at the optimum coagulant dosage. The slurry from the coagulation process was used to study the sludge sedimentation time under optimized initial pH and coagulant dose. To study the effect of initial organic load on coagulation, wastewater sample was diluted in different ratios and coagulation study was carried out under optimized conditions of pH and PAC dosage. The removal efficiency for other parameters i.e. chlorophenolics, cRFA, AOX, and BOD was determined under optimized conditions.

### 2.3. Analytical methods

Fourier transform infrared (FTIR) spectrum for PAC was recorded in the range 400–4,000 $cm^{-1}$ by a NICOLET 6700 spectrophotometer (Thermo Scientific) using KBr pellets. Wastewater samples were analyzed immediately in the laboratory for pH, COD, BOD, color, AOX, chlorophenolics, and cRFA. Color measurement was performed spectrometrically on a Analytic Jena spectrophotometer (Spekol 2000). COD and BOD estimation were done by the standard methods [34]. AOX was determined by Dextar AOX analyzer (Thermo Electron Corporation).

Gas chromatography–mass spectrometry (GC–MS) was used for the qualitative and quantitative analysis of chlorophenolics in the wastewater. The extraction of various chlorophenolics was done as per the procedure suggested by Lindstrom and Nordin [35]. The chlorophenolics were converted to readily volatile acetyl derivatives prior to GC–MS analysis [36]. The analysis of various chlorophenolics as acetyl derivatives was performed on GC coupled with MS (Trace GC Ultra-DSQ, Thermo Electron Corporation). The derivatized sample was injected into the TR-5 fused silica capillary column using an auto sampler (AI 3,000, Thermo Electron Corporation).

The GC oven temperature was held at 45℃ (1 min) and raised to 280℃ at 6℃/min, keeping the final temperature for 25 min. Injector, mass transfer line, and ion source temperatures were set at 210, 280, and 200℃, respectively. The carrier gas used was helium (He) at a flow rate of 1 mL/min. MS was operated in the electron impact ionization mode with an ionizing energy of 70 eV. The various chlorophenolics were first identified by matching their mass spectrum with that obtained from the NIST library. Once main peaks were identified, pure standard solutions of target compounds (as acetyl derivatives) were injected into the GC–MS for determining the retention times (RT) of respective chlorophenolics.

GC was used for the qualitative and quantitative analysis of cRFA. The extraction of cRFA from wastewater was achieved as suggested by Voss and Rapsomatiotis [37]. The cRFA were converted to their readily volatile methyl esters prior to GC analysis. Methylation was done with diazomethane according to the procedure suggested by Vogel [38]. After extraction, all samples of cRFA as methyl esters were injected into the Optima-1-MS fused silica capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness) and were analyzed using GC (Trace GC Ultra, Thermo Electron Corporation). The detector used for this purpose was a flame ionization detector at 10° range. The GC oven temperature was held at 190℃ (4 min) and increased to 210℃ at 1℃/min, from 210 to 230℃ at 2℃/min, from 230 to 250℃ at 3℃/min, keeping the final temperature 250℃ for 15 min. Injector and detector temperatures were set at 300℃. The carrier gas used was nitrogen ($N_2$) at a flow rate of 1 mL/min. Target compounds were identified by comparing RT with those of derivatized standards and quantified with the help of response factor of the specific compound.

## 3. Results and discussion

### 3.1. Characterization of PAC

FTIR spectrum of PAC (Fig. 1) shows the bands at 3,439 and 1,615 $cm^{-1}$ which are associated with OH vibrations [39]. Particularly, the band at 3,439 $cm^{-1}$ is due to the $^{-}$OH stretching vibration of hydroxyls and the band at 1,615 $cm^{-1}$ is due to the bending vibration of water molecules in the structure of Al polycations [40]. The bands at 1,113 and 956 $cm^{-1}$ are assigned to the bending vibrations of Al–$OH_2$ and the band at 653 $cm^{-1}$ is assigned to the symmetric stretching mode of Al–O bond of the central $AlO_4^-$ in $Al_{13}$ molecule [41]. Furthermore, metal complexes containing oxo groups exhibit absorption bands at the region 1,100–900 $cm^{-1}$ [39]; therefore, the low intensity bands at 956 and 653 $cm^{-1}$ could be assigned to vibrations of these types of bonds. The 3,600 and 3,300 $cm^{-1}$ bands are assigned to the OH stretch of Al–OH–Al in the polymer. The different frequencies of the bands are indicative of two different locations for OH in the polymer; however, no specific structural assignments are proposed [42].

### 3.2. Optimization of process parameters

#### 3.2.1. Wastewater characteristics

During the optimization of process parameters for coagulation-flocculation studies, the wastewater was characterized in terms of pH, COD, and color. The average values for pH, COD, and color were 8.1 ± 0.4, 1,723 ± 186 mg/L, and 5,449 ± 515 Pt–Co mg/L, respectively. The wastewater was alkaline in nature with dark brown in color and high organic load. The high concentration of color was mainly contributed by lignin and its derivative compounds.

#### 3.2.2. PAC dosage optimization

In order to determine the optimum dosage for the removal of COD and color from paper mill

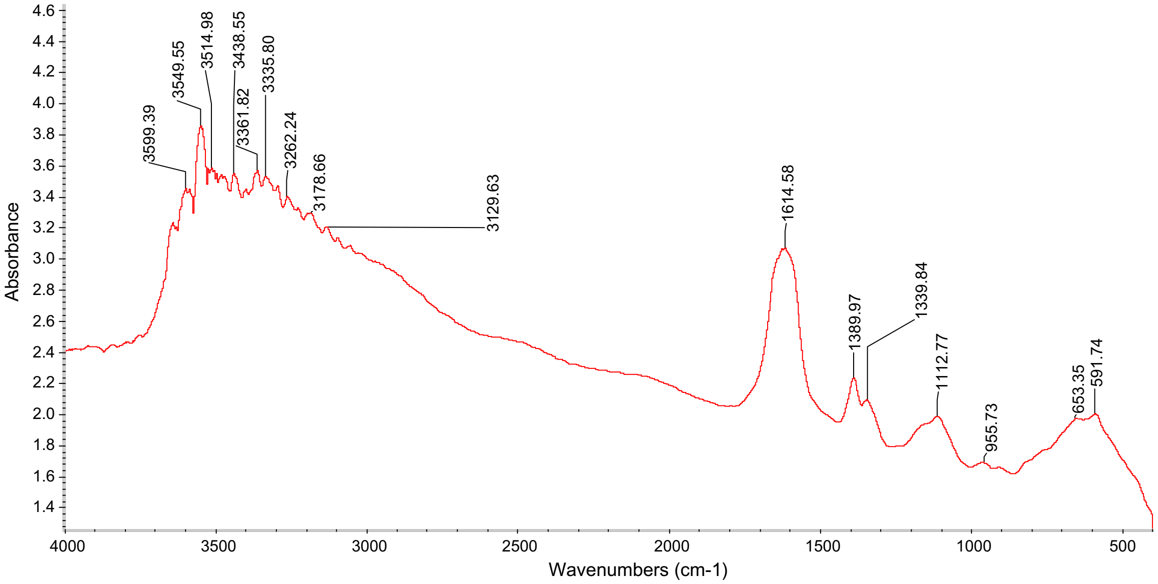

Fig. 1. FTIR spectrum of PAC.

wastewater, different dosages of PAC were used (0.5–4.5 mg/L). The initial pH value of the wastewater samples was adjusted to 7.0 before coagulation. Fig. 2 shows the effect of PAC dosage on COD and color removal efficiency. It was observed that percent COD and color removal increased as the PAC dosage increased from 0.5 to 2.5 g/L giving maximum COD and color removal efficiency of 69.1 and 98%, respectively. The increase in COD and color removal efficiency is due to increase in the concentration of various hydrolysis species which destabilize the colloidal particles present in the paper mill wastewater. Due to further increase in PAC dosage, the color removal efficiency became constant and the COD removal efficiency decreased slightly then finally became constant. Excessive amount of coagulant dosage causes re-dispersion of colloidal particles [31]. The nature of organic matter has a significant effect on the coagulant dose. For the wastewater with high molar mass organic matter, the optimal coagulant dose is expected to be low because the removal mechanism is mainly charge neutralization, however, if organic matter consists of low molar mass substances, the removal mechanism is expected to be adsorption onto metal hydroxide surfaces and optimal coagulant dose is thus much larger for treatment [43].

Fig. 3 shows the final pH of the wastewater (supernatant). The final pH of the supernatant decreased from 6.8 to 3.8 as PAC dosage varied from 0.5 to 4.5 g/L. This decrease in pH of supernatant is due to the acidic character of $Al^{3+}$. By reacting with $OH^-$ ions, $Al^{3+}$ precipitates in the form of $Al(OH)_3$ [44].

PAC generates multivalent aluminium ions which neutralized the colloidal particles. The hydrolyzed aluminium flocs enmesh the colloids and drive to settle. The removal of COD and color is mainly by charge neutralization and adsorption. PAC contains a significant fraction of highly polynuclear species, such as $Al_2O_4(OH)_{24}^{7+}$, which remain comparatively stable for a long time after dosing. These polynuclear hydroxide products are more readily associated with organic compounds than monomeric hydrolysis products, thus more effective for neutralizing the negative charge of functional groups on the surface of organic matter [45].

At 1.5 g/L of PAC dosage, the percentage of COD and color removal was 65.9 and 96.2%, respectively. But it was found that as the PAC dosage increased from 1.5 g/L to 2.5 g/L, only marginal increase in COD (about 3%) and color (about 2%) removal efficiency were observed. Hence, 1.5 g/L PAC was selected as the optimum dosage for subsequent studies.

### 3.2.3. *pH optimization*

Fig. 4 represents the effect of initial pH on the removal of COD and color, respectively, for the PAC dosage of 1.5 g/L. It was observed that COD and color removal efficiency increased as the initial pH of the wastewater increased from 4.0 to 8.0, giving maximum COD and color removal efficiency of 67.9

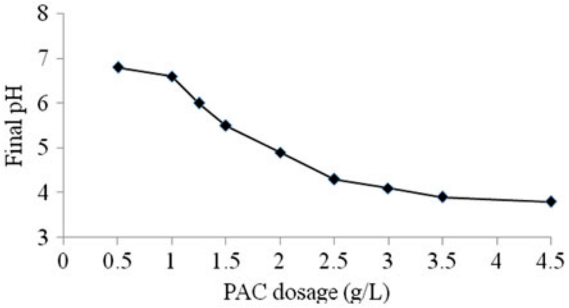

Fig. 3. Effect of PAC dosage on final pH of paper mill wastewater.

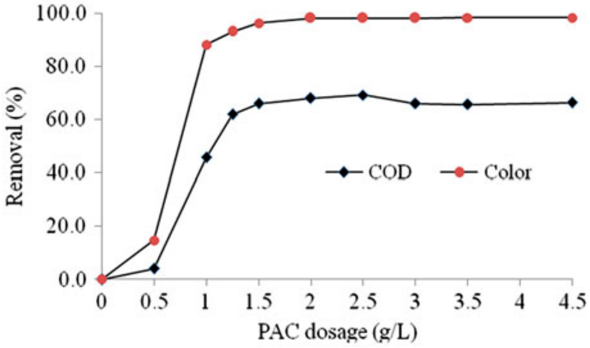

Fig. 2. Effect of PAC dosage on COD and color removal of paper mill wastewater.

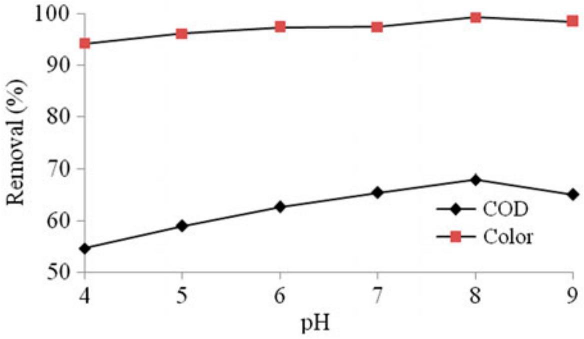

Fig. 4. Effect of initial pH on COD and color removal of paper mill wastewater.

and 99.2%, respectively. But, further increase in initial pH from 8.0 to 9.0 decreases the COD and color removal efficiency slightly. For pH > 8, the decrease in the removal efficiency of COD and color may be due to the $Al(OH)^{-}_{4}$ ions. Speciation of Al(III) shows that aluminum present in the water is in the form of $Al(OH)^{-}_{4}$ ions for pH > 8 [46]. These ions reduce the COD and color removal by PAC due to electrostatic repulsion between negatively charged colloidal particles present in the paper mill wastewater and $Al(OH)^{-}_{4}$ ions. Adin and Asano found that at pH values between 6 and 9, aluminum coagulation occurs through the mechanism of physical attachment of particles in the mass of the aluminum hydroxide precipitate i.e. by sweep coagulation [47].

Fig. 5 shows the effect of initial pH on the final pH of wastewater for PAC dosage 1.5 g/L. The final pH of the supernatant decreased from 6.3 to 3.9 as the initial pH varied from 9.0 to 4.0. It can be seen that final pH was less than the initial pH in full studied range. It is well known that the addition of PAC leads to release of $H^+$ ions which results in the decrease of pH for the wastewater [46,48,49].

On the bases of above results, initial pH 8.0 was taken as optimum pH for the further experiments.

### 3.2.4. Settling time

Fig. 6 shows the settling of slurry produced by the coagulation process in terms of the sludge-supernatant interface height as a function of settling time. During the first 30 min, a rapid decrease in the height of the sludge-supernatant interface was observed. Thereafter, in the transition settling period i.e. from 30 to 90 min, slow settling of sludge was observed with time. After 90 min, no significant change in the height of the sludge-supernatant interface took place. For further experiments, slurry settling time of 90 min was considered as optimum.

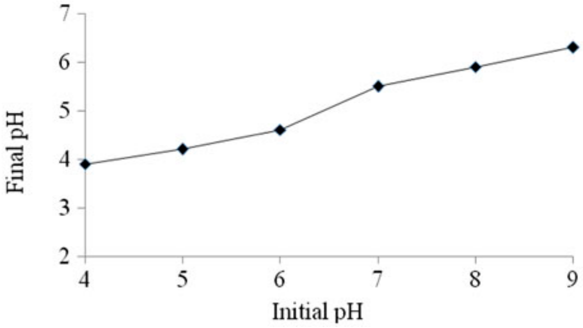

Fig. 5. Effect of initial pH and final pH of wastewater for PAC dosage 1.5 g/L.

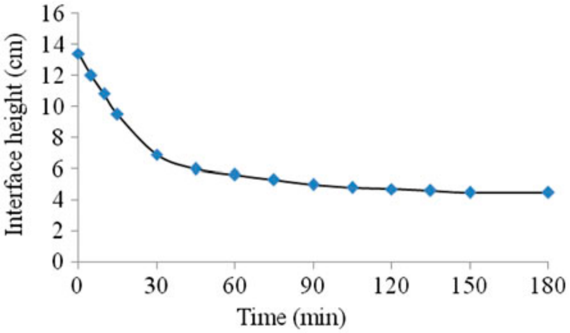

Fig. 6. Settling curve of slurry from the coagulation of paper mill wastewater by PAC.

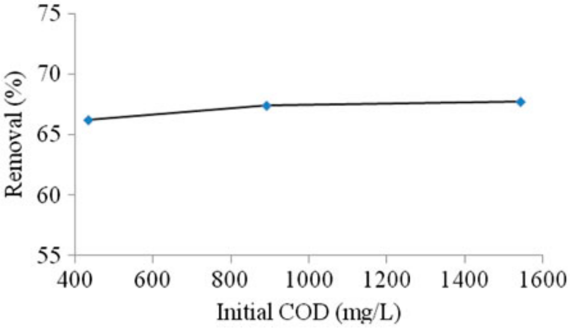

Fig. 7. Effect of initial COD load on COD removal efficiency. Initial pH 8.0, PAC dosage 1.5 g/L, and contact time 90 min.

### 3.2.5. Effect of organic load

Fig. 7 shows the effect of initial COD load on COD removal efficiency for the PAC dosage of 1.5 g/L and initial pH 8.0. The initial COD of the wastewater varied from 433 to 1,543 mg/L. Examination of data shows that the initial COD load had no significant effect on the removal COD efficiency. Srivastava et al. also reported the similar findings for the paper mill wastewater treatment with PAC [32]. This shows that our results are in good agreement with the literature.

## 3.3. Treatment

On the bases of optimization results, treatment of paper mill wastewater was conducted under optimum conditions of pH (8.0), dosage of PAC (1.5 g/L), and slurry settling time (90 min) to know the treatment efficiency of coagulant for the removal of AOX, BOD, COD, color, chlorophenolics, and cRFA from paper mill wastewater. Fig. 8 shows the chromatogram of chlorophenolics and cRFA in untreated and PAC treated wastewater.

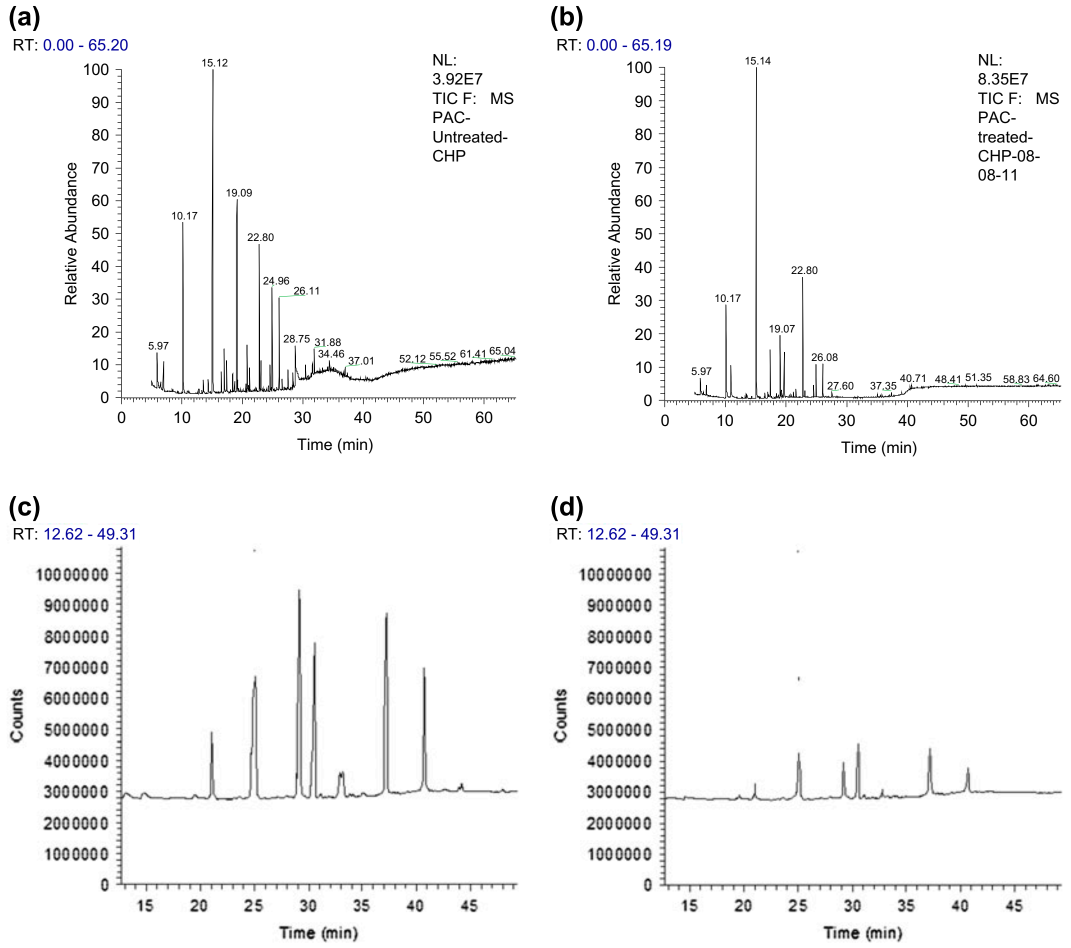

Fig. 8. Chromatogram of chlorophenolics: (a) and cRFA (c) in untreated wastewater; chromatogram of chlorophenolics (b) and cRFA (d) in PAC treated wastewater.

### 3.3.1. Wastewater characteristics

For the coagulation-flocculation treatment studies, the characteristics of untreated wastewater in terms of pH, COD, color, BOD, AOX, chlorophenolics, and cRFA are shown in Table 1. The organic load and color of the wastewater were low as compared to the wastewater used in the optimization process. Tables 2 and 3 show the concentration of individual chlorophenolics and cRFA, respectively.

Table 2 shows that 19 categories of 4 chlorophenolic compounds (CP, CC, CG, and CSA) were detected in the untreated wastewater. Among the various chlorophenolics, 2,4,5-TCP contributed to the highest concentration (28.20 ± 1.60 μg $L^{-1}$) followed by 2,5-DCP (4.82 ± 0.28 μg $L^{-1}$), 4,5-DCG (4.68 ± 0.28 μg $L^{-1}$), 3,6-DCC (4.00 ± 0.11 μg $L^{-1}$), 4-CG (3.00 ± 0.25 μg $L^{-1}$), 2,4-DCP (1.59 ± 0.06 μg $L^{-1}$), 3-CP (1.40 ± 0.06 μg $L^{-1}$), and 2,6-DCP (1.15 ± 0.08 μg $L^{-1}$). Other chlorophenolics were present in minor quantities.

Examination of data of total chlorophenolics content reveals that CP contributed to the highest share with 75.1% followed by CG (16.6%), CC (7.7%), and CSA (0.7%) as shown in Fig. 9(a). Fig. 9(b) shows the percentage of chlorophenolics on the basis of chlorine atom substitution. Trichlorophenolics (TCP) contributed to the highest share with 57.2% followed by dichlorophenolics (DCP) (32.8%), monochlorophenolics

Table 1
Characteristics of pulp and paper mill wastewater

| Parameter | Average value ± SD |
|---|---|
| pH | 7.3 ± 0.06 |
| COD (mg $L^{-1}$) | 1,267 ± 24.0 |
| Color (Pt-Co mg $L^{-1}$) | 2,706 ± 57 |
| $BOD_5$ (mg $L^{-1}$) | 345 ± 13 |
| AOX (mg $L^{-1}$) | 18.3 ± 0.35 |
| Chlorophenolics (μg $L^{-1}$) | 52.2 ± 2.56 |
| cRFA (μg $L^{-1}$) | 87.2 ± 6.03 |

Table 2
Removal of chlorophenolics from paper mill wastewater by PAC (1.5 g/L)

| S. no. | Name of compound | Concentration (µg L$^{-1}$) | Removal (%) |
|---|---|---|---|
| 1. | 3-CP | 1.40 ± 0.06 | 26.4 |
| 2. | 4-CP | 0.57 ± 0.07 | 30.2 |
| 3. | 2,6-DCP | 1.15 ± 0.08 | ND |
| 4. | 2,5-DCP | 4.82 ± 0.28 | 38.7 |
| 5. | 2,4-DCP | 1.59 ± 0.06 | 25.7 |
| 6. | 3,4-DCP | 0.11 ± 0.03 | ND |
| 7. | 4-CG | 3.00 ± 0.25 | 19.7 |
| 8. | 2,4,5-TCP | 28.20 ± 1.60 | 51.1 |
| 9. | 2,3,6-TCP | 0.65 ± 0.07 | 91.5 |
| 10. | 2,3,5-TCP | 0.15 ± 0.04 | 22.8 |
| 11. | 4,5-DCG | 4.68 ± 0.28 | 13.5 |
| 12. | 2,3,4-TCP | 0.52 ± 0.05 | 65.3 |
| 13. | 4,6-DCG | 0.42 ± 0.03 | 23.5 |
| 14. | 3,6-DCC | 4.00 ± 0.11 | 23.3 |
| 15. | 3,4,6-TCG | 0.14 ± 0.02 | ND |
| 16. | 3,4,5-TCG | 0.05 ± 0.02 | 17.4 |
| 17. | 4,5,6-TCG | 0.11 ± 0.03 | 17.4 |
| 18. | TeCG | 0.25 ± 0.25 | ND |
| 19. | 2,6-DCSA | 0.35 ± 0.03 | ND |

Table 3
Removal of cRFA from paper mill wastewater by PAC

| S. no. | Compound | Concentration (µg L$^{-1}$) | Removal (%) |
|---|---|---|---|
| 1. | DCSA$^{a}$ | 26.56 ± 1.23 | 91.0 |
| 2. | CDAA$^{b}$ | 17.87 ± 1.33 | 85.9 |
| 3. | DCDA$^{b}$ | 23.40 ± 1.29 | 79.9 |
| 4. | TCSA$^{a}$ | 19.40 ± 2.19 | 89.1 |

[a] Chloro fatty acids.
[b] Chloro resin acids.

(MCP) (9.5%), and tetrachlorophenolics (TeCP) (0.5%). Pentachlorophenol was not detected in the untreated wastewater. The results indicate that about 99.5% of the identified compounds in the untreated wastewater were MCP, DCP, and TCP compounds. It shows that these compounds are predominant in untreated pulp and paper mill wastewater. The relative quantities of various chlorophenolics present in the wastewater mainly depend on the bleaching conditions (i.e. bleaching sequence used, bleach chemical dose, temperature for bleaching), nature and characteristics of lignin, wood species, and type of pulp employed in bleaching by the paper mill.

The quantities of various cRFA detected in the untreated wastewater are shown in Table 3. Two chloro fatty acids (cFA) i.e. 9,10-dichlorostearic acid (DCSA) and 9,10,12,13-tetrachlorostearic acid (TCSA) and two chloro resin acids (cRA) i.e. chlorodehydroabietic acid (CDAA) and 12,14-dichlorodehydroabietic acid (DCDA) were identified in the untreated wastewater of paper mill wastewater. Among all cRFA, the concentration of DCSA was found to be highest (26.56 ± 1.23 µg L$^{-1}$) followed by DCDAA (23.40 ± 1.29 µg L$^{-1}$), TCSA (19.40 ± 2.19 µg L$^{-1}$), and CDAA (17.87 ± 1.33 µg L$^{-1}$). The results indicate that the total content of cFA was higher in comparison to cRA in the untreated wastewater. cFA and cRA contributed to 52.7 and 47.3%, respectively, of the total cRFA content.

### 3.3.2. Wastewater treatment by PAC

The treatment efficiency of the coagulant was examined by monitoring various pollution parameters in the untreated and treated wastewater, and the obtained results are demonstrated in Tables 1–3 and in Figs. 9–11.

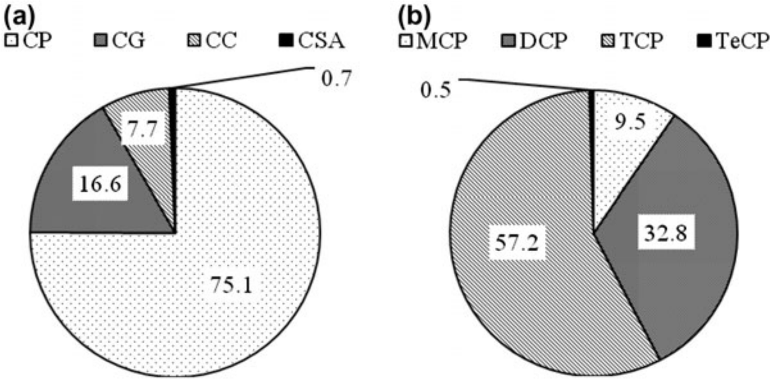

Fig. 9. Percentage of chlorophenolics detected in the paper mill wastewater: (a) according to chemical family, and (b) according to attached chlorine atom.

Fig. 10(a) shows the average percent removal of BOD, COD, and color from paper mill wastewater by coagulation/flocculation treatment process. For BOD, COD, and color removal, efficiency of PAC were 49, 68, and 97%, respectively. It was observed that the removal efficiency for color was higher in comparison to BOD and COD. This is due to the presence of aluminium oxide in PAC, which is known to act as a good adsorbent for the color. Dhakhwa et al. reported the percentage of COD and color reduction were up to 86 and 97%, respectively, by using PAC (1.2 g/L) as coagulant, from synthetic pulp and paper mill wastewater [20]. In our study, the color reduction is comparable with the above literature but the COD reduction is low. This may be due to the different wastewater characteristics, as in our case wastewater was procured from the paper mill and it contains a magnitude of organic and inorganic compounds. Under optimized conditions, Srivastava et al. reported the reduction of 80% COD and 90% color from paper mill wastewater by using PAC as coagulant [32]. The PAC reduced COD by 83% and color by 92% from paper mill wastewater at an optimum pH of 5.0 and a coagulant dose of 8 mL $L^{-1}$ [33].

Fig. 10(b) shows the average percent removal of chlorophenolics, AOX, and cRFA. The removal of chlorophenolics, AOX, and cRFA obtained by PAC was 41, 66, and 87%, respectively. Among chlorinated compounds, the highest removal was observed for cRFA.

After coagulation treatment process with PAC, 14 chlorophenolic (out of 19) compounds were detected in the wastewater. 14–100% removal of chlorophenolics was achieved as shown in Table 2. The chlorophenolics i.e. 2,6-DCP, 3,4-DCP, 3,4,6-TCG, TeCG, and 2,6-DCSA were not detected after treatment. Examination of the data shows that the removal efficiency by PAC treatment was 47% for CP, 20% for CG, 23% for CC, and 100% for CSA (as shown in Fig. 11(a)). Lowest removal was observed for CG and CC. Fig. 11(b) shows the removal of chlorophenolics (according to Cl atom attached) by the PAC treatment. Percentage removal of MCP, DCP, TCP, and TeCP were 23, 26, 52, and 100%, respectively. The removal efficiency for different cRFA was varied from 80–91% as shown in Table 3. The highest removal was observed for DCSA (91%) followed by TCSA (89%), CDAA (86%), and DCDA (80%). Treatment efficiency of PAC was better for the removal of cFA (90%) than cRA (83%).

While the treatment with PAC, complete removal of CSA and TeCP was observed as compared to other chlorophenolics. This may be due to the lowest share of CSA (0.7%) and TeCP (0.5%) in untreated

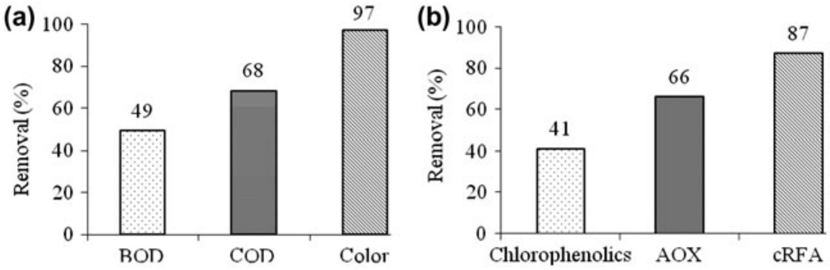

Fig. 10. (a) Percentage removal of BOD, COD, and color by PAC (b) percentage removal of chlorophenolics, AOX, and cRFA by PAC.

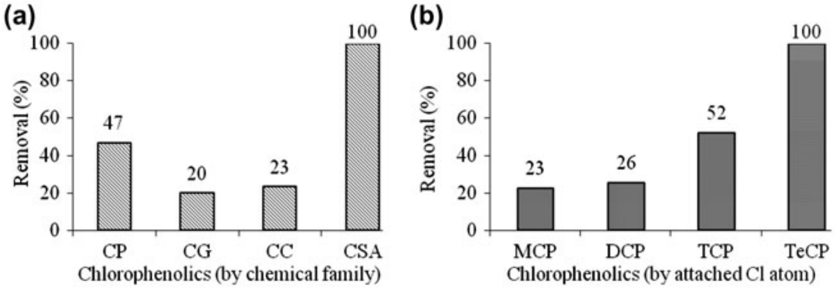

Fig. 11. Percentage removal of chlorophenolics by PAC: (a) according to chemical family, and (b) according to attached chlorine atom.

wastewater compared to other categories. The removal of higher chlorinated chlorophenolics was higher as compared to lower chlorinated chlorophenolics. This may be due to the higher negative charge on the highly chlorinated chlorophenolics. More the chlorine atoms more will be the negative charge on the chlorophenolic compound in the wastewater and this favors the coagulation process. Removal of higher chlorinated chlorophenolics (TCP and TeCP) by PAC also favors to reduce the toxicity of paper mill wastewater as these compounds are more toxic in comparison to lower chlorinated chlorophenolics (MCP and DCP). Examination of results shows that during the treatment process, the removal of cRA (83%) was found to be low as compared to cFA (90%). This difference in the treatment efficiency may be due to the complex structure (aromatic) of cRA as compared to cFA which has linear chain structure. It was also observed that the removal efficiency for cRFA was higher in comparison to chlorophenolics. The molecular size of cRFA is large as compared to chlorophenolics which favors the flocculation process [50]. The hydrophobic fraction of organic matter is generally removed in coagulation more efficiently than the hydrophilic fraction. Furthermore, high molar mass compounds are more readily removed than low molar mass compounds [51–53] most likely because high molar mass compounds are quite hydrophobic in nature [54].

The data regarding the treatment of chlorinated compounds (AOX, chlorophenolics, and cRFA) from paper mill wastewater by PAC are not available in the literature. Sharma and Kumar reported the removal of chlorophenolics (45–55%) from laboratory-generated effluent of mixed wood pulp by using different coagulants (alum, ferric chloride, ferric alum) and γ-alumina as adsorbent [21].

After treatment with PAC, the BOD and COD values of the wastewater were still above the Indian standard BOD and COD discharge limits of 30 and 250 mg/L, respectively. The BOD/COD ratio increased from 0.272 to 0.433 due to the higher removal of COD (68%) load in comparison to BOD (49%). On the other hand, the removal of highly chlorinated chloro-organics was higher as compared to lower ones, which reduced the toxicity of wastewater. There was no specific standard discharge limits for color and different chloro-organics. The above-mentioned results indicate that the PAC treatment is not sufficient to discharge the paper mill wastewater directly and further treatment is required to meet out the discharge limits. It can be recommended that PAC treated wastewater is suitable for biological treatment as the biodegradability of the wastewater was increased and toxicity was decreased.

## 4. Conclusions

Based on the present investigation, it can be concluded that PAC is effective coagulant for the treatment of pulp and paper mill wastewater. The removal of color and COD by PAC increases as the initial pH of the wastewater and coagulant dosage increases till it attains equilibrium. The optimum initial pH of wastewater and dosage for PAC was 8.0 and 1.5 g/L, respectively. The results show a removal efficiency range between 41–68% for chlorinated phenolics, AOX, BOD, and COD. For cRFA, the removal efficiency was comparatively higher (87%). Among different parameters, the highest removal of color (97%) was observed from wastewater by PAC. Coagulation by PAC results in the complete removal of CSA and TeCP from paper mill wastewater. It was observed that PAC is more effective for the removal of highly chlorinated chlorophenolics as compared to lower ones. The PAC treatment is not sufficient to discharge the pulp and paper mill wastewater directly and further treatment is required to meet out the discharge limits. It can be recommended that PAC treated wastewater is suitable for biological treatment as the biodegradability of the wastewater increases and toxicity decreases after treatment.

## Acknowledgment

The research grant for this study provided by the Ministry of Environment and Forest, Government of India is gratefully acknowledged.

## References

[1] E.C. Catalkaya, F. Kargi, Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study, J. Hazard. Mater. B. 139 (2007) 244–253.

[2] E.C. Catalkaya, F. Kargi, Advanced oxidation treatment of pulp mill effluent for TOC and toxicity removals, J. Environ. Manag. 87 (2008) 396–404.

[3] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater a review, Sci. Tot. Environ. 3 (2004) 37–58.

[4] P. Bajpai, P.K. Bajpai, Biological color removal of pulp and paper mill wastewaters, J. Biotechnol. 33 (1994) 211–220.

[5] C.W. Dence, D.W. Reeve, Pulp Bleaching—Principles and Practice, TAPPI Press, Atlanta, GA, 1996.

[6] G.S. Furman, D.B. Easty, Chlorination of dehydroabietic acid under pulp bleaching conditions, TAPPI J. 67 (1983) 89.

[7] C. Sharma, S. Mahanty, S. Kumar, N.J. Rao, Gas chromatographic determination of pollutants in the chlorination and caustic extraction stage effluent from the bleaching of a bamboo pulp, Talanta. 44 (1997) 1911–1918.

[8] C.S.R. Freire, A.J.D. Silvestre, C.P. Neto, Carbohydrate derived chlorinated compounds in ECF bleaching of hardwood pulps: Formation, degradation and contribution to AOX in a bleached kraft pulp mill, Environ. Sci. Technol. 37 (2003) 811–814.
[9] D.V. Savant, R.A. Rahman, D.R. Ranadi, Anaerobic digestion of absorbable organic halides (AOX) from pulp and paper industry wastewater, Bio. Technol. 30 (2005) 30–40.
[10] R.H. Voss, J.T. Wearing, R.D. Mortimer, T. Kovacs, A.L. Wong, Chlorinated organics in kraft bleachery effluents, Pap. ja Puu. 62 (12) (1980) 809–814.
[11] T.R. Stuthridge, K. Johnsen, H. Hoel, J. Tana, Bioaccumulation of resin acids in trout exposed to thermomechanical pulping effluents and their receiving waters, 49th Appita Annual General Conference Proceedings, Appita, Carlton, Australia, 1995, pp. 533–538.
[12] G. Erisction, A. Larsson, DNA—A dots in perch (*Perca fluviatillis*) in coastal water pollution with bleachening pulp mill effluents, Ecotoxicol. Environ. Saf. 46 (2000) 167–173.
[13] R. Orrego, J. Guchardi, L. Beyger, R. Krause, D. Holdway, Comparative embryo toxicity of pulp mill extracts in rainbow trout (*Oncorhynchus mykiss*), American flagfish (*Jordanella floridae*) and Japanese medaka (*Oryzias latipes*), Aquat. Toxicol. 104 (2011) 299–307.
[14] M.H. Priha, E.T. Talka, Biological activity of bleached kraft mill effluent (BKME) fractions and process streams, Pulp Pap. Can. 87 (1986) 143–147.
[15] H.A. Aziz, Z. Daud, M.N. Adlan, Y.T. Hung, The use of polyaluminium chloride for removing color, COD and ammonia from semi-aerobic leachate, Int. J. Environ. Eng. 1 (1) (2009) 20–35.
[16] S. Ghafari, H.A. Aziz, M.J.K. Bashir, The use of polyaluminum chloride and alum for the treatment of partially stabilized leachate: A comparative study, Desalination. 257 (2010) 110–116.
[17] I. Lou, S. Gong, X. Huang, Y. Liu, Coagulation optimization for low temperature and low turbidity source water using combined coagulants: A case study, Desalin. Water Treat. 46 (2012) 107–114.
[18] N.D. Tzoupanos, A.I. Zouboulis, Novel inorganic-organic composite coagulants based on aluminium, Desalin. Water Treat. 13 (1) (2010) 340–347.
[19] M.T. Samadi, M.H. Saghi, A. Rahmani, J. Hasanvand, S. Rahimi, M.S. Syboney, Hamadan landfill leachate treatment by coagulation-flocculation process, Iran. J. Environ. Health. Sci. Eng. 7 (3) (2010) 253–258.
[20] S. Dhakhwa, S. Bandyopadhyay, A. Garg, Removal of color and COD from synthetic paper mill effluent using coagulation/acid precipitation process, IPPTA. J. 23 (2) (2011) 187–191.
[21] C. Sharma, S. Kumar, Removal of chlorinated phenols, from (C+E) effluents of mixed wood pulp by flocculants and adsorbent, Elixir Pollution. 37 (2011) 3673–3677.
[22] J. Zhao, W. Lin, Q. Chang, W. Liu, S. Wang, Y. Lai, Effects of operational conditions on the floc formation time and rate in magnesium hydroxide coagulation process, Desalin. Water Treat. 45 (2012) 153–160.
[23] P. Jarvis, B. Jefferson, S.A. Parsons, Characterising natural organic matter flocs, Water Sci. Technol. 4 (4) (2004) 79–87.
[24] A. Amirtharajah, C.R. O'Melia, Coagulation Processes: Destabilization, Mixing and Flocculation, Water Quality and Treatment, 4th ed., American Water Works Association, McGraw Hill, 1990.Please provide the name of the city of publication for Refs. [24,48].
[25] M. Rebhun, M. Lurie, Control of organic matter by coagulation and floc separation, Water Sci. Tech. 27 (11) (1993) 1–20.
[26] S. Sinha, Y. Yoon, G. Amy, J. Yoon, Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes, Chemosphere. 57 (2004) 1115–1122.
[27] N.D. Tzoupanosa, A.I. Zouboulisa, C.A. Tsoleridis, A systematic study for the characterization of a novel coagulant (polyaluminium silicate chloride) , Colloids and Surfaces A: Physicochem. Eng. Aspects. 342 (2009) 30–39.
[28] P.M. Bertsch. Aqueous polynuclear aluminum species. in: G. Sposite, (Ed.), The Environmental Chemistry of Aluminum, CRC Press, Boca Raton, FL, 1989, pp. 87–115.
[29] J.Q. Jiang, N.J.D. Graham, Pre-polymerised inorganic coagulants and phosphorus removal by coagulation—a review, Water SA. 24 (3) (1998) 237–244.
[30] H.X. Tang, Z.K. Luan, Features and mechanism for coagulation flocculation process of polyaluminum chloride, J. Environ. Sci. 7 (2) (1995) 204–211.
[31] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, IWA Publishing, London,2006.
[32] V.C. Srivastava, I.D. Mall, I.M. Mishra, Treatment of pulp and paper mill wastewaters with poly aluminium chloride and bagasse fly ash , Colloids and Surfaces A: Physicochem. Eng. Aspects. 260 (2005) 17–28.
[33] P.K. Chaudhari, B. Majumdar, R. Choudhary, D.K. Yadav, S. Chand, Treatment of paper and pulp mill effluent by coagulation, Environ. Technol. 31 (4) (2010) 357–363.
[34] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC,1998.
[35] K. Lindstrom, J. Nordin, Gas chromatographic mass spectrometry of chlorophenols in spent bleach liquors, J. Chromat. A. 128 (1976) 13–26.
[36] K. Abrahamsson, T.M. Xie, Direct determination of trace amount of chlorophenols in fresh water, waste water and sea water, J. Chromat. A. 279 (1983) 199–208.
[37] R.H. Voss, A. Rapsomatiotis, An improved solvent extraction based procedure for the GC analysis of resin and fatty acids in pulp mill effluents, J. Chromat. 346 (1985) 205–214.
[38] A. Vogel, A Textbook on Practical Organic Chemistry, 3rd ed., English Language Book Society, London, 1975.
[39] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds—Part A: Theory and Applications in Inorganic Chemistry, 5th ed., John Wiley and Sons, New York, 1997.
[40] J.T. Kloprogge, R.L. Frost, Raman and infrared spectroscopic investigation of the neutralization of aluminium in the presence of monomeric orthosilicic acid, Spectrochim. Acta A. 55 (1999) 1359–1363.

[41] J.T. Kloprogge, H. Ruan, R.L. Frost, Near-infrared spectroscopic study of basic aluminium sulphate and nitrate, J. Mater. Sci. 36 (2001) 603–607.

[42] D.A. Riesgraf, M.L. May, Infrared spectra of aluminum hydroxide chlorides, Appl. Spectroscopy. 32 (4): (1978) 362–366.

[43] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, Adv. Colloid Interface Sci. 159 (2010) 189–197.

[44] T.R. Hundt, C.R. O'Melia, Aluminum-fulvic acid interactions: Mechanisms and applications, J. AWWA. 80 (4) (1988) 176–186.

[45] Y. Zhou, Y. Wang, Z. Liang, Decolorization and COD Removal of Yeast Wastewater by Coagulation Process Using Poly-Aluminum Chloride, Taylor and Francis Group, London, 2007.

[46] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[47] A. Adin, T. Asano, The role of physical-chemical treatment in wastewater reclamation and reuse, Water Sci. Tech. 37 (10) (1998) 79–90.

[48] M.M. Benjamin, Water Chemistry, International Edition, McGraw Hill, 2002.

[49] D. Wang, W. Sun, Y. Xu, H. Tang, J. Gregory, Speciation stability of inorganic polymer flocculant-PACl, Colloids Surfaces A: Physicochem. Eng. Asp. 243 (2004) 1–10.

[50] L. Yang, B. Sun, W. Huang, Study on removal of organics of different molecular weight by coagulation-membrane filtration process, J. Sustain. Develop. 3 (1) (2010) 191–196.

[51] C.W.K. Chow, J.A. van Leeuwen, R. Fabris, M. Drikas, Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon, Desalination. 245 (2009) 120–134.

[52] G. Korshin, C.W.K. Chow, R. Fabris, M. Drikas, Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights, Wat. Res. 43 (2009) 1541–1548.

[53] E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, Impact of fractional character on the coagulation of NOM, Colloids Surfaces A: Physicochem. Eng. Asp. 286 (2006) 104–111.

[54] M. Szlachta, W. Adamski, Effects of natural organic matter removal by integrated processes: Alum coagulation and PAC-adsorption, Wat. Sci. Technol. 59 (10) (2009) 1951–1957.